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Full paper

Absorption Cross Section Simulation: a Preliminary Study of Ultraviolet Absorption Spectroscopy for Ozone Gas Measurement

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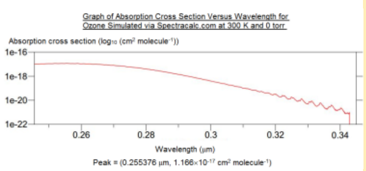
Graphical abstract



Abstract

Preliminary study to measure gaseous ozone concentration using ultraviolet absorption spectroscopy is presented. Firstly, background of ozone is introduced. Next, fundamental theory behind ultraviolet absorption spectroscopy is discussed based on Beer-Lambert's Law and absorption spectrum of ozone. After that, absorption cross section of ozone is simulated via spectralcalc.com. Temperature of system is varied. Peak absorption cross section and peak absorption wavelength are found to be 1.166×10^{-21} m^2 $molecule^{-1}$ and 255.376 nm respectively at 300 K and 0 torr. Absorption cross section in ultraviolet region shows slight variation of at most 1.286 per cent when temperature is changed from 200 K to 300 K. Around room temperature, peak absorption cross section simulated in current work is consistent with previous work, because relative error is found to be small in between 1.630 per cent and 3.087 per cent. Unlike previous work, absorption of light by ozone is detected in ultraviolet region only due to weak absorption in visible region.

Keywords: Absorption spectroscopy; absorption cross section; ultraviolet; ozone gas; spectralcalc.com

Abstrak

Kajian awal untuk mengukur kepekatan gas ozon menggunakan spektroscopi penyerapan ultraungu dibincangkan. Latar belakang ozon diperkenalkan. Prinsip di sebalik kaedah pengukuran ini dibincangkan menerusi Hukum Beer-Lambert dan spektrum penyerapan ozon. Spectrum penyerapan ozon dikira menerusi laman spectralcalc.com. Suhu dimanipulasikan. Hasil kajian menunjukkan puncak keratan rentas penyerapan adalah 1.166×10^{-21} m^2 $molekul^{-1}$ pada 255.376 nm, 300 K dan 0 torr. Perubahan puncak keratan rentas penyerapan di zon ultraungu adalah tidak lebih daripada 1.286 peratus apabila suhu diubah dari 200 K hingga 300 K. Dalam lingkungan suhu bilik, perbandingan puncak keratan rentas penyerapan antara kajian ini dengan kajian sebelumnya memuaskan, kerana ralat dikenalpasti berada di antara 1.630 peratus dan 3.087 peratus. Penemuan yang bercanggahan dengan kajian sebelumnya ialah penyerapan cahaya oleh ozon hanya dikenalpasti pada zon ultraungu kerana penyerapan cahaya yang lemah di zon boleh dilihat.

Kata kunci: Spektroskopi penyerapan; keratan rentas penyerapan; ultraungu; gas ozon; spectralcalc.com

■1.0 INTRODUCTION

"Good up high, bad nearby" is the description of ozone by Environment Protection Agency of United States in 2003 [1]. This is because ozone at stratosphere protects earthy lives from harmful ultraviolet rays from the sun, but ozone at troposphere is a pollutant. Ozone, O_3 is formed by combination of three oxygen atoms. Although ozone is colourless at low concentration, it has distinctive smell. Breathing in ozone is bad for respiratory system [2]. In addition, ozone speeds up paint wear and damages vegetation [3]. Despite that, ozone, if is used properly, can be useful due to its strong oxidising property and environmentally friendly features. Ozone can be applied in gas phase or made soluble in water. The lower the temperature, the higher the solubility [4]. The unstable molecule quickly reverts to oxygen; therefore, it must be generated on site. For instance, ozone may be generated via dielectric barrier discharge [5] on demand.

■2.0 PRINCIPLE OF MEASUREMENT

Beer-Lambert's Law is the fundamental theory behind ultraviolet absorption spectroscopy. Typical experiment setup can be found in literature [6]. Light emitted from a broadband light source is partially absorbed by ozone and received by a spectrometer. The relationship is found in the literature [7]:

$$A = \sigma N_A c_i l_s = \varepsilon c_i l_s = \ln(I_0/I_t) = -\ln T_r \qquad (1)$$

A is optical density, optical depth or absorbance
σ is absorption cross section of sample in m^2 $molecule^{-1}$
N_A is Avogadro's constant, 6.022×10^{23} molecule mol^{-1}
c_i is concentration of sample gas of interest in mol m^{-3}
l_s is optical path length of sample
ε is molar absorption coefficient in m^2 mol^{-1}
I_0 is light intensity on sample
I_t is light intensity through sample
T_r is transmittance of light

Based on Equation 1, absorbance (A) is dependent on concentration (c_i), absorption cross section (σ) and optical path length (l_s). These three parameters causes intensity of light to decrease from I_0 to I_t.

2.1 Absorption Spectrum of Ozone

According to Figure 1, absorption spectrum of ozone has a large peak in ultraviolet region (Hartley band) and a small in peak visible region (Chappuis band). Absorption cross section of ozone in visible region (4.14×10^{-25} m^2 $molecule^{-1}$) [9] is reported to be more than two thousand times smaller than typical absorption cross section of ozone in ultraviolet region. According to Table 1, peak absorption wavelength in ultraviolet region is typically selected at mercury resonance wavelength at 253.65 nm [10, 11, 12, 13, 14] Absorption cross sections in ultraviolet region that are applied previously range from 1.13×10^{-21} m^2 $molecule^{-1}$ [10] to 1.147×10^{-21} m^2 $molecule^{-1}$ [14]. This shows disagreement among different authors. This poses difficulty to researcher to select appropriate absorption cross section to calculate ozone concentration accurately using Equation 1. Conducting experiment at peak absorption wavelength is important so that sensor is sensitive to concentration change. Therefore, primary study of ozone sensor is dedicated to simulate peak absorption cross section via spectralcalc.com. The software is a subscription based online high resolution spectral modelling developed by GATS Inc. [15].

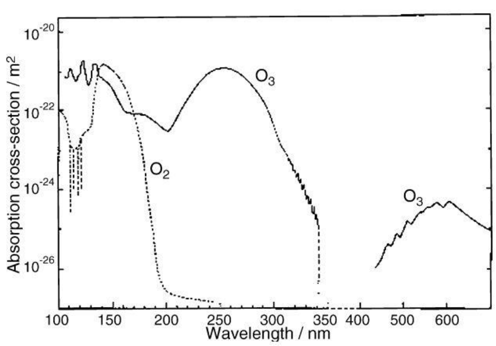


Figure 1 Graph of absorption cross section of ozone per molecule versus wavelength [8]

■3.0 SIMULATION METHODOLOGY

Figure 2 shows input of spectralcalc.com to calculate absorption cross section. Firstly, line list browser in spectralcalc.com is clicked. In this simulation, HITRAN 2008 cross section database is selected. Gas selected for simulation is ozone gas only. Spectral range set for the simulation is from 245.5 nm to 700 nm to determine absorption cross section of ozone in both ultraviolet and visible regions. In the simulator, pressure is fixed at 0 torr. Temperature of gas is set at 300 K. Then, simulation is repeated for temperature at 280K, 260K, 240K, 220K and 200 K respectively.

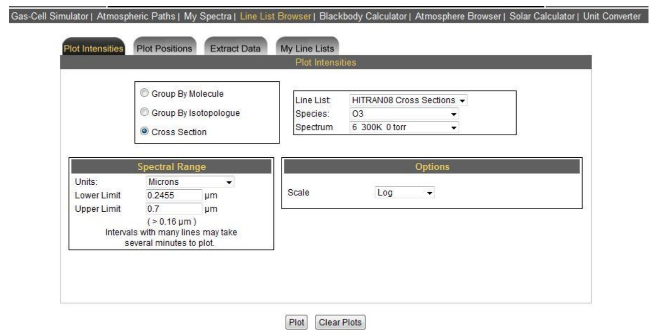


Figure 2 Graphic user interface of line list browser in spectralcalc.com

■3.0 RESULTS AND DISCUSSIONS

Simulation results are tabulated in Table 1 and illustrated in Figure 3, Figure 4 and Figure 5 as follow:

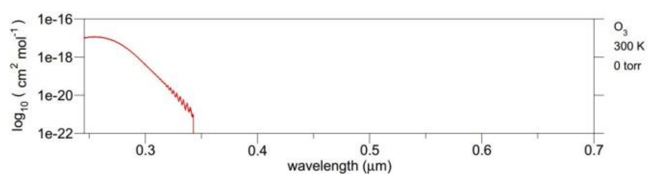


Figure 3 Absorption cross section per molecule in logarithmic scale of ozone versus wavelength from 245.5 nm to 700 nm at 300 K and 0 torr

Figure 3 shows simulation result in current work. Absorption cross section in ultraviolet region is strongly detected. Compared to previous work in Figure 1 [8], peak at visible region is not noticeable in current work. This is because absorption cross section in ultraviolet region is very much higher than that of visible region.

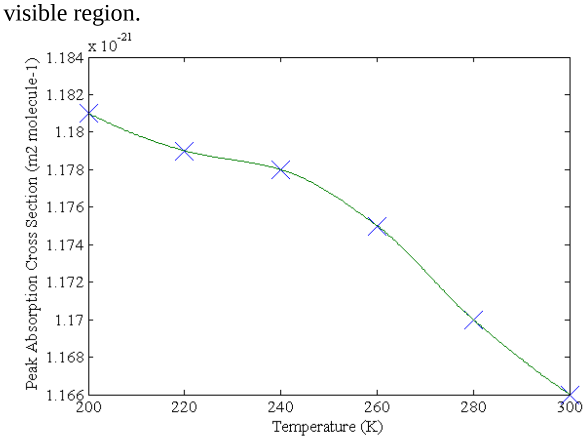


Figure 4 Graph of peak absorption cross section of gaseous ozone versus temperature at pressure of 0 torr

Figure 4 shows the higher the temperature, the lower the absorption cross section. The finding is consistent with previous work [10, 12, 16]. Deviation between maximum point (σ_{200K} = 1.181 × 10^{-21} m^2 molecule^{-1}) and minimum point (σ_{300K} = 1.166 × 10^{-21} m^2 molecule^{-1}) is 1.286 per cent. It is calculated via (σ_{200K}-σ_{300K})/σ_{300K} × 100,where σ_{200K} and σ_{300K} are absorption cross sections at 200 K and 300 K respectively. Therefore, we conclude that peak absorption cross sections of ozone in ultraviolet region stay almost constant within temperature range from 200 K to 300 K. The finding agrees well with previous work [10, 12] (deviation of at most 1 per cent from 218 K to 295 K) and [16] (deviation of 1.3 per cent from 203 K to 298 K).

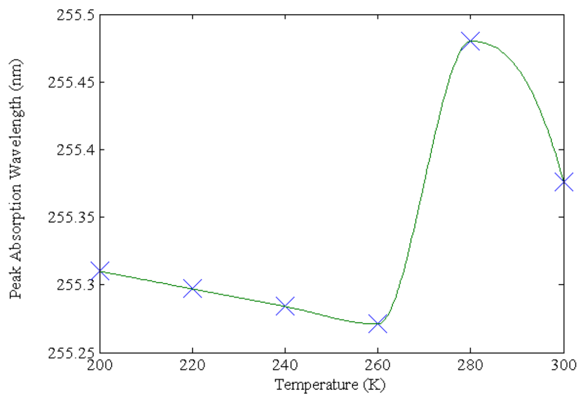


Figure 5 Graph of peak absorption wavelength of gaseous ozone versus temperature at pressure of 0 torr

Figure 5 shows peak absorption wavelengths are very close to each other from 200 K to 300 K. The values range from 255.271 nm to 255.48 nm and has mean of 255.34 nm. This agrees well with literature [10, 12, 16] that temperature dependence at Hartley band is small.

Table 1 shows absorption cross section simulated at 300 K in current work (1.166 × 10^{-21} m^2 molecule^{-1}) is comparable to that of previous work at room temperature. Absorption cross section in literature [14] (1.147 × 10^{-21} m^2 molecule^{-1}) is in close agreement with current work. Error of previous work relative to current work ranges from 1.630 per cent to 3.087 per cent. Absorption cross section obtained in current work is slightly larger than previous work. The discrepancy may be due to difference in temperature in current work simulation and previous work experiment. Hence, we conclude that ozone has strong absorption in ultraviolet region at 300 K, particularly at wavelength 255.376 nm.

■4.0 FURTHER WORK

Further work is required to verify simulated peak absorption cross section of ozone via experiment. Simulation is done at 0 torr, but experiment may not be practically done at vacuum. Furthermore, temperature of actual experiment may vary from simulation temperature, 300 K. Peak absorption wavelength and peak absorption cross section to be obtained via experiment are expected to deviate slightly from simulation due to temperature and pressure difference.

■5.0 CONCLUSION

In conclusion, simulation of ozone absorption cross section via spectralcalc.com is done. Simulation results show peak absorption cross section is 1.166 × 10^{-21} m^2 molecule^{-1} at 255.376 nm, 300 K and 0 torr. Deviation of absorption cross section is at most 1.286 per cent when temperature is changed from 300 K to 200 K. Temperature effect at Hartley band is negligible as long as ozone is measured at peak absorption wavelength near average of 255.34 nm. Absorption cross section simulated in current work is in close agreement with previous work, due to small relative error of 1.630 per cent to 3.087 per cent. Current work suggests measurement of ozone in ultraviolet region, because absorption cross section of ozone in visible region is too small to be noticed in simulation. Validity of absorption cross sections simulated in current work should be further verified via experiment.

Table 1 Comparison of absorption cross section between current work and previous work

Researchers	[10]	[11]	[12]	[13]	[14]	Current work					
Temperature (K)	295	295	295	293	295	300	280	260	240	220	200
Peak absorption wavelength (nm)	253.65	253.65	253.65	253.65	253.65	255.376	255.48	255.271	255.284	255.297	255.31
Peak absorption cross section (m^2 molecule^{-1})	1.13 ×10^{-21}	1.1305 ×10^{-21}	1.1305 ×10^{-21}	1.137 ×10^{-21}	1.147 ×10^{-21}	1.166 ×10^{-21}	1.17 ×10^{-21}	1.175 ×10^{-21}	1.178 ×10^{-21}	1.179 ×10^{-21}	1.181 ×10^{-21}
Relative error (%)[c], $\|(\sigma_{[n]}-\sigma_{300K})/\sigma_{300K}\| \times 100$	3.087	3.045	3.045	2.487	1.630	-	-	-	-	-	-

[c] $\sigma_{[n]}$ is absorption cross section in previous work experiment. σ_{300K} is absorption cross section in current work simulation at 300K via spectralcalc.com

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References

[1] United States Environmental Protection Agency. 2003. *Ozone, Good Up High, Bad Nearby*. United States Environmental Protection Agency. Office of Air and Radiation. Washington. Access online on 28 May 2013 from www.epa.gov/airnow/gooduphigh/ozone.pdf.

[2] Jakpor, O. 2007. Pulmonary Effects of Ozone-Generating Air Purifiers. *Young Scientists Journal*. 7: 20–31.

[3] Arif, N. L. and Abdullah, A. M. 2011. Ozone Pollution and Historical Trends of Surface Background Ozone Level: A Review. *World Applied Sciences Journal 14 (Exploring Pathways to Sustainable Living in Malaysia: Solving the Current Environmental Issues)*. 31–38.

[4] Sonntag, C. V. and Gunten, U. V. 2012. *Chemistry of Ozone in Water and Wastewater Treatment*. IWA Publishing. United Kingdom.

[5] Salam, Z., Facta M. and Amjad, M. 2013. Transformerless Power Supply Based on Single Switch Resonant Inverter for Ozone Generation. *Applied Power Electronics Conference and Exposition (APEC), 2013 Twenty-Eighth Annual IEEE*. 3330–3333.

[6] O'Keeffe, S., Fitzpatrick, C. and Lewis, E. 2007. An Optical Fibre Based Ultra Violet and Visible Absorption Spectroscopy System for Ozone Concentration Monitoring. *Sensors and Actuators B: Chemical*. 125(2): 372–378.

[7] Hughes, H. K. 1963. Beer's Law and the Optimum Transmittance in Absorption Measurements. *Applied Optics*. 2(9): 937–945.

[8] Campbell, I. M. 1986. *Energy and the Atmosphere: A Physical-Chemical Approach.* Second Edition. John Wiley & Sons Ltd.

[9] Teranishi, K., Shimada, Y., Shimomura, N. and Itoh, H. 2013. Investigation of Ozone Concentration Measurement by Visible Photo Absorption Method. *Ozone: Science & Engineering: The Journal of the International Ozone Association*. 35(3): 229–239.

[10] Brion, J., Chakir, A., Daumont, D., Malicet, J. and Parisse, C. 1993. High-resolution Laboratory Absorption Cross Section of O3. Temperature Effect. *Chemical Physics Letters*. 213(5–6): 610–612.

[11] Daumont, D., Brion, J., Charbonnier, J. and Malicet, J. 1992. Ozone UV Spectroscopy I: Absorption Cross-Sections at Room Temperature. *Journal of Atmospheric Chemistry*. 15(2): 145–155.

[12] Malicet, J., Daumont, D., Charbonnier, J., Parisse, C., Chakir, A. and Brion, J. 1995. Ozone UV Spectroscopy. II. Absorption Cross-Sections and Temperature Dependence. *Journal of Atmospheric Chemistry*. 21(3): 263–273.

[13] Voigt, S., Orphal, J., Bogumil, K. and Burrows, J. P. 2001. The Temperature Dependence (203–293 K) of the Absorption Cross Sections of O3 in the 230–850 nm Region Measured by Fourier-transform Spectroscopy. *Journal of Photochemistry and Photobiology A: Chemistry*. 143(1): 1–9.

[14] Hearn, A. G. 1961. The Absorption of Ozone in the Ultra-violet and Visible Regions of the Spectrum. *Proceedings of the Physical Society*. 78: 932.

[15] GATS, Inc. *SpectralCalc.com, High-resolution Spectral Modeling*. Access online on 29 May 2013 from http://www.spectralcalc.com/info/about.php.

[16] Paur, R. J. and Bass A. M. 1985. The Ultraviolet Cross-Sections of Ozone: I. The Measurements. Ozone Symposium-Greece 1984. *Atmospheric Ozone*. 606–610.